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RHEOLOGY OF CLAYS FROM THE TROITSKOE DEPOSIT

Yu. I. Goncharov,[1] E. A. Doroganov,[1] and K. V. Zhidov[1]

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The rheological properties of clays from the Troitskoe deposit are investigated. It is established that this clay contains kaolinite characterized by a disordered structure, which leads to increased viscosity and poor liquescence. The introduction of clay from the Malo-Arkhangel'skoe deposit makes it possible to achieve a satisfactory efflux time.

The problems of expanding material sources and improving the quality of argillaceous materials are becoming quite topical. The expansion of material sources, as a rule, takes the form of using local materials, which can meet technological requirements only after special preparation and concentration procedures. Therefore, studying the physicochemical and technological specifics of argillaceous materials acquires special significance.

Among the physicochemical and technological properties of argillaceous materials, the rheological parameters of clay suspensions (slips) play an important role. Therefore, the studies of the clay – water system are needed to control the processing of clay materials and to molding ceramic products using different technologies. As a rule, most technologies require aqueous suspensions with a maximum possible fluidity and a sufficiently high content of the solid phase. The specified conditions call for a detailed investigation of the structural specifics of mineral phases and the effect of the ionic composition of disperse systems on dispersing colloid clay systems, especially the ones with an increased capacity for coagulation.

The purpose of the present work is to further study the rheological properties of slips based on clays from the Troitskoe deposit, whose application in fine ceramics is rather doubtful. The studies were based on core clay samples from the elevation interval of 6 – 13 m.

Macroscopically this clay is a bluish-gray rock with numerous veins and interlayers of yellowish-brown and gray-brown colors represented by iron hydroxides and jarosite. The clay is weakly sandy (quartz content 30 – 40%) and belongs to the kaolinite-illite type with montmorillonite impurities [1].

Rheological properties were determined using a Rheotest-2 rotational viscosimeter with coaxial cylinders. Average layer samples were taken by the quartering method with an interval of 1 m. The clay was initially milled in a ball mill up to completely passing through a No. 008 sieve and then slips were prepared using a propeller mixer. The first stage of analysis was carried out with moisture 55%, which is the reference moisture for preparing a slip of density 1.63 – 1.65 g/cm^3. Later the research was continued in the moisture interval of 53 – 65%. The initial study of the flow properties of slips used distilled water as the dispersion medium.

The deflocculating agents were the following liquefiers: sodium tripolyphosphate (Na TPP), rheotan, solution of sodium water glass (density 1.36 g/cm^3, silica modulus 2.4), soda ash, distillers' spent grains slop, lignotin, lignosulfonate FKhLS-M, tannin, sodium oxalate, sodium fluoride, polyvinyl alcohol solution, and carboxymethyl cellulose solution.

Electrolytes were introduced into the slip in an amount of 0.01 – 0.5 wt.% converted to dry matter. After the electrolyte was introduced, gravitational mixing of the slip was performed in a ball mill with a small number of milling bodies for 20 min. The effect of electrolytes was estimated based on the time of efflux of 100 ml of slip from the VZ-246 viscosimeter with an opening diameter of 4 mm. The efflux time was measured after 30 sec and 30 min of exposure in the viscosimeter.

It is established that with 55% moisture none of the slips is fluid without introducing an electrolyte. This is due to the high shear stress value P_k required for the start of the deformation. It can be seen from the rheograms shown in Fig. 1 that the lowest P_k equal to 40 Pa is registered in the slip of the clays taken from 6 – 7 m elevation, whereas P_k in the slip of the clay taken from 12 – 13 m is higher and equal to 66 Pa. The highest shear stress required for the destruction of the thixotropic structure (122 Pa) is registered in the slip of the clay taken from 9 – 10 m level.

The analysis of various electrolytes indicated that the most effective is Na TPP, whereas other liquefiers cannot produce a slip with a first efflux time less than 25 sec. Thus,

[1] V. G. Shukhov Belgorod State Technological University, Belgorod, Russia.

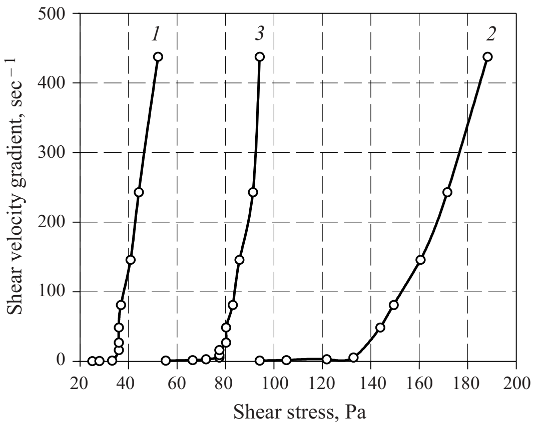

Fig. 1. Rheological characteristics of Troitskoe clay taken from the levels of 6 – 7 m (*1*), 9 – 10 m (*2*), and 12 – 13 m (*3*).

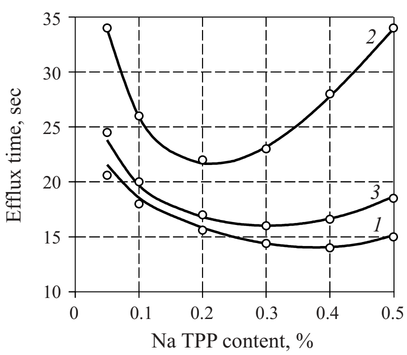

Fig. 2. Dependence of slip efflux time on electrolyte content for Troitskoe clay bedded at the level of 6 – 7 m (*1*), 9 – 10 m (*2*), and 12 – 13 m (*3*).

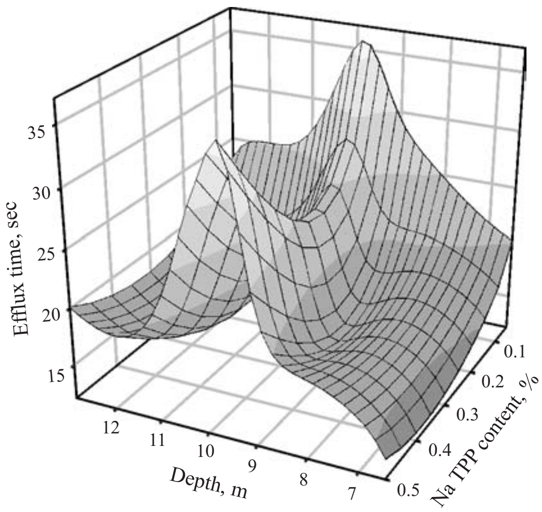

Fig. 3. Slip efflux time for varying electrolyte content and bedding depth of Troitskoe clay.

for the slip of the clay taken from 6 – 7 m the introduction of 0.1% Na TPP decreases its P_k 4.5-fold, the addition of 0.2% makes it 35 times lower, and 0.3% makes it 180 times lower. The shear stress in the slip of clay from 12 – 13 m elevation decreases in the similar way. Less obvious is this effect on the slip of clay from 9 – 10 m. Upon introducing 0.2% Na TPP the shear stress decreases 15 times, and with 0.3% it decreases 36 times.

Figure 2 shows the slip fluidity (after 30 sec) curves of clays taken from different levels depending on the amount of Na TPP additive. Upon introducing 0.1% electrolyte, the efflux time of the slip of the clay taken from 6 – 7 m is 17.5 sec; as the additive content grows to 0.4% the efflux time decreases to 14 sec, then, as the Na TPP content grows to 0.5%, the efflux time increases to 15 sec. The slip of clay taken from 12 – 13 m elevation behaves similarly, but its efflux time is significantly longer. The slip of clay from 9 – 10 m, due to its highest viscosity, has an increased efflux time, and its minimum of 22 – 23 sec is registered in the fluidity curve with an electrolyte content of 0.2 – 0.3%. An increase in electrolyte content to 0.5% increases the efflux time to 34 sec.

The thickening coefficient of the slips determined on the basis of the efflux time after 30 min changes similarly to the viscosity variation.

The full representation of the variation of clay fluidity for different levels of occurrence depending on the quantity of Na TPP introduced is shown in Fig. 3. The response surface of the dependence obtained indicates that an anomalous increase in the slip efflux tine is observed when approaching the elevation of 9 – 10 m. This dependence to a different extent is observed in the whole variation ranges of the content of the liquefying additive.

These modifications in rheological properties are the consequences of the specific mineralogical composition of clays considered. Calculations based on the differential thermal analysis data showed that the content of kaolinite in the clay considered changes depending on the depth of occurrence (Fig. 4) At the same time, the variations in kaolinite content depending on depth virtually coincides with fluidity variations, i.e., the maximum kaolinite content (33%) is registered at the level of 9 – 10 m.

The results of the x-ray phase analysis of clays corroborate the assumption that kaolinite contained in the clay composition has a disordered structure [1]. This is confirmed by the diffraction patterns of Troitskoe clay and (for comparison purposes) well-crystallized Glukhovetskoe kaolin shown in Fig. 5. According to the data in [2], an indication of kaolinite with a perfect structure is partial resolution of doublets $11\bar{1}$ and $\bar{1}11$ corresponding to d/n = 4.18 and 4.13 Å. The reflections in the interplanar distance interval of 3.5 – 2.5 Å have the index k equal to 1 or 2. Their presence points to a high degree of crystallization. In the case of significant disordering, no other reflections are observed along the axis b between reflections 002 (d = 3.57 Å) and 201 (d = 2.65 Å). Kaolinite with a perfect crystalline structure exhibits four clearly defined reflections in this interval.

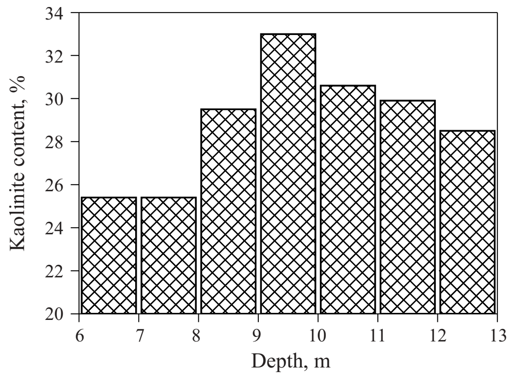

Fig. 4. Variation of kaolinite content versus the depth of bedding of the Troitskoe clay.

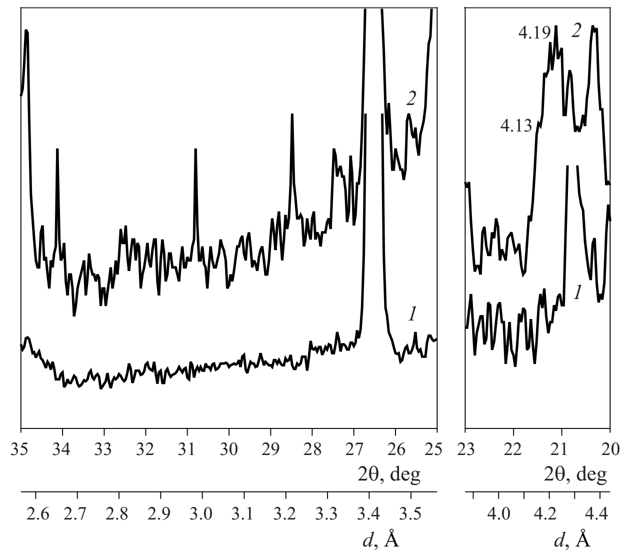

Fig. 5. Diffraction patterns of Troitskoe clay (*1*) and Glukhovetskoe kaolin (*2*) samples.

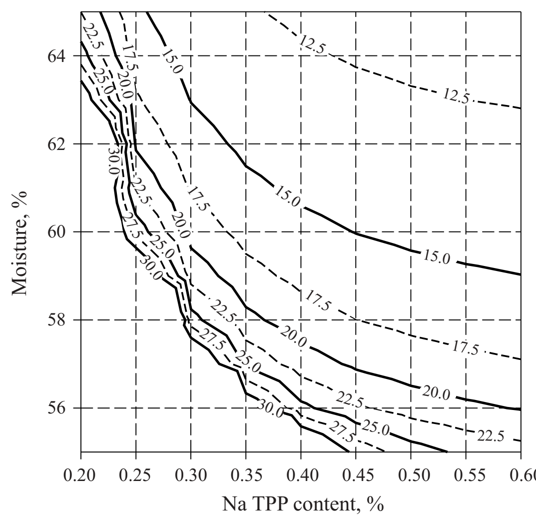

Fig. 6. Efflux time (in sec, indicated on the curves) of slip based on Troitskoe clay with varying moisture and electrolyte content.

In subsequent studies the dispersion medium was technical water, i.e., the circulating water used at the factory for slip preparation. The ionic composition of technical water is as follows: (mg · equ/liter): 6.02 Ca^{2+}, 3.20 Mg^{2+}, 0.44 K^{+}, 3.41 Na^{+}, 9.60 OH^{-}, 2.40 Cl^{-}, 1.29 SO_4^{2-}; pH = 8.52. A specific feature of this technical water is a substantial quantity of coagulant ions, which has a negative effect on the liquescence of clay slips. The ionic composition of an aqueous clay extract shows that the clay contains few soluble salts, consequently, their effect on clay liquescence is insignificant.

A comparative analysis of the rheological characteristics of slips of clays from elevations of 6 – 7, 9 – 10, and 12 – 13 m based on distilled and technical water shows that the use of the latter decreases the deformation velocity in the whole shear stress interval. It results in increasing slip viscosity and efflux time. However, it should be noted that the total trend of slip viscosity variation according to the occurrence levels does not change, which points to the prevailing effect of the specific mineralogical composition on clay liquescence.

To develop the technological parameters of Troitskoe clay liquescence, a sample averaged for the whole bedding section was used.

Figure 6 shows the variation of efflux time depending on Na TPP content and moisture for the averaged clay sample. The obtained results make it possible to identify the concentration range of Na TPP additive and relative moisture to obtain a slip with preset fluidity. Thus, the initial efflux time equal to 20 sec after 30 sec exposure is reached by the following combinations of Na TPP additive and moisture (%): 0.2 Na TPP – slip moisture over 65.0, 0.25 – 62.0, 0.3 – 59.5, 0.4 – 57.5, and 0.5 – 56.5, respectively.

For the purpose of decreasing the slip moisture and the amount of electrolyte additive, easily liquefying clay was additionally introduced into the slip. We investigated slips containing additives of 15, 25, and 40% Malo-Arkhangel'skoe clay in combinations with 0.25 and 0.30% Na TPP additives. The moisture corresponding to the required fluidity was determined for the above compositions. It was found that introducing 15% Malo-Arkhangel'skoe clay makes it possible to decrease the moisture of the slip with comparable Na TPP quantities from 59.5 – 60.0 to 57.0 – 58.0%. With 0.25% Na TPP the necessary fluidity is ensured by the slip moisture of 61 – 62%.

An increase in the amount of this clay to 25% decreases the moisture to 55.5 – 56.0% with 0.30% Na TPP and makes it possible to obtain a fluid slip of moisture 57.5 – 58.0% with 0.25% Na TPP. A further increase in the content of Malo-Arkhangel'skoe clay to 40% decreases the slip moisture to 54.5 – 55.0% with 0.25% Na TPP. It should be noted that the introduction of well-liquefying clay in the amount of 15 to 40% significantly decreases the slip thickening coefficient (from 1.5 to 1.2).

The use of the same content of rheotan or a mixture of rheotan with Na TPP as electrolyte to a lesser extent decreases the viscosity of the slips considered. In this case we could not achieve satisfactory values of efflux time.

Thus, a comparative analysis of the rheological properties of slips demonstrates that effective viscosity consistently increases with increasing depth of clay occurrence and reaches its maximum at the level of 9 – 10 m, after which viscosity gradually decreases. This regularity is traced within the entire shear velocity gradient when distilled or technical water is used as the dispersion medium with electrolytes introduced. The slips investigated have abnormally high values of shear stress required for the destruction of the thixotropic structure.

Clay from the Troitskoe deposit contains kaolinite that has a disordered structure and a high moisture capacity; moreover, its content in clay increases in the middle part of the section (elevation of 9 – 10 m). The presence of kaolinite with an imperfect crystalline structure is responsible for the abnormally high efflux time. This is the main reason for poor liquescence of Troitskoe clays.

The introduction of clay from the Malo-Arkhangel'skoe deposit (up to 40%) makes it possible to decrease the slip moisture to 54.5 – 55.0%, decrease thickening, and achieve a satisfactory efflux time.

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